Example – model for van der Waals interactions

The vdW interaction is the main force between closed-shell systems (atoms or molecules) without permanent dipole moments, such as rare gas atoms or CH_4 molecules. We will use a model of two H atoms at large separation, which gives the main features of such forces, including the well-known R^{-6} dependence. The purpose is to demonstrate a non trivial, realistic perturbation treatment and the considerations made in its application.

The system consists of two H atoms, one with nucleus a and electron 1, the other with b and 2. The distance R between the nuclei is large relative to interatomic distances, $R \gg r_{a1}, r_{b2}$. Ignoring the interaction between the atoms, the Hamiltonian is

$$H^{(0)} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{r_{a1}} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_{b2}}.$$

$H^{(0)}$ is separable to Hamiltonians of two H atoms, so we know the solutions,

$$H^{(0)}\psi_{n_1 l_1 m_1}(a1)\psi_{n_2 l_2 m_2}(b2) = \left(E_{n_1} + E_{n_2}\right)\psi_{n_1 l_1 m_1}(a1)\psi_{n_2 l_2 m_2}(b2)$$

where ψ_{nlm} is a function of an H atom. The interaction between the two atoms is the perturbation,

$$H^{(1)} = -\frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}.$$

The $H^{(1)}$ terms are small relative to $H^{(0)}$, since the denominators are large. The first task is to express $H^{(1)}$ in R and intra-atomic distances, which will make possible a large–small separation. If the molecular axis is chosen as the z coordinate,

$$r_{12} = \sqrt{(x_{b2} - x_{a1})^2 + (y_{b2} - y_{a1})^2 + (z_{b2} + R - z_{a1})^2}$$

$$r_{a2} = \sqrt{x_{b2}^2 + y_{b2}^2 + (z_{b2} + R)^2}$$

$$r_{b1} = \sqrt{x_{a1}^2 + y_{a1}^2 + (z_{a1} - R)^2}.$$

Using the Taylor expansion $\frac{1}{\sqrt{1+\epsilon}} = 1 - \frac{\epsilon}{2} + \frac{3}{8}\epsilon^2 + \cdots$, we will collect terms to second power in x_{a1} etc. Note: this will include all terms coming from $\frac{1}{2}\epsilon$, but only some terms from $\frac{3}{8}\epsilon^2$.

$$\frac{1}{r_{12}} = \frac{1}{R} \frac{1}{\sqrt{1 + \frac{2(z_{b2}-z_{a1})}{R} + \frac{(x_{b2}-x_{a1})^2+(y_{b2}-y_{a1})^2+(z_{b2}-z_{a1})^2}{R^2}}}$$

$$\approx \frac{1}{R}\left(1 - \frac{2R(z_{b2} - z_{a1}) + (x_{b2} - x_{a1})^2 + (y_{b2} - y_{a1})^2 + (z_{b2} - z_{a1})^2}{2R^2}+\right.$$

$$\left.+\frac{3}{8}\frac{4(z_{b2} - z_{a1})^2}{R^2}\right)$$

$$= \frac{1}{R}\left(1 - \frac{2R(z_{b2} - z_{a1}) + (x_{b2} - x_{a1})^2 + (y_{b2} - y_{a1})^2 - 2(z_{b2} - z_{a1})^2}{2R^2}\right)$$

Similarly,

$$\frac{1}{r_{a2}} \approx \frac{1}{R}\left(1 - \frac{2Rz_{b2} + x_{b2}^2 + y_{b2}^2 - 2z_{b2}^2}{2R^2}\right)$$

$$\frac{1}{r_{b1}} \approx \frac{1}{R}\left(1 - \frac{-2Rz_{a1} + x_{a1}^2 + y_{a1}^2 - 2z_{a1}^2}{2R^2}\right)$$

$$\frac{1}{R} = \frac{1}{R}.$$

$H^{(1)}$ is obtained by adding up the 4 equations with appropriate signs. The terms with 1 in the parentheses cancel out, as do terms with Rz in the numerator. The largest terms remaining are with coordinates squared:

$$H^{(1)} = \frac{e^2}{R^3} \left(x_{a1}x_{b2} + y_{a1}y_{b2} - 2z_{a1}z_{b2} \right).$$

This is the well-known interaction between the two dipoles $e\,\vec{r}_{a1}$ and $e\,\vec{r}_{b2}$.

The first-order correction $E_{1s1s}^{(1)}$ vanishes:

$$\langle \psi_{1s1s}^{(0)}|x_{a1}x_{b2}|\psi_{1s1s}^{(0)}\rangle = \langle \psi_{1s}(a1)|x_{a1}|\psi_{1s}(a1)\rangle \langle \psi_{1s}(b2)|x_{b2}|\psi_{1s}(b2)\rangle,$$

and each of the integrals vanishes because of parity. The same holds for y and z integrals.

Second order:

$$\lambda^2 E_{1s1s}^{(2)} = \sum_{k \neq 1s1s} \frac{\langle \psi_{1s1s}^{(0)}|H^{(1)}|\psi_k^{(0)}\rangle \langle \psi_k^{(0)}|H^{(1)}|\psi_{1s1s}^{(0)}\rangle}{E_{1s1s}^{(0)} - E_k^{(0)}}.$$

An approximate value may be found analytically. The denominator is $-\frac{e^2}{a_0}\left(1 - \frac{1}{2n_1^2} - \frac{1}{2n_2^2} \right)$, where n_1, n_2 cannot be both equal to 1. Replacing the denominator by $-e^2/a_0$, it may be moved out of the summation:

$$E_{1s1s}^{(2)} \approx -\frac{1}{e^2/a_0} \sum_{k \neq 1s1s} \langle \psi_{1s1s}^{(0)}|H^{(1)}|\psi_k^{(0)}\rangle \langle \psi_k^{(0)}|H^{(1)}|\psi_{1s1s}^{(0)}\rangle.$$

The term with $k = 1s1s$ is zero, so we have a complete sum, and the unit operator may be dropped to give

$$E^{(2)}_{1s1s} \approx \sum_k \langle \psi^{(0)}_{1s1s} | \left(H^{(1)} \right)^2 | \psi^{(0)}_{1s1s} \rangle.$$

Taking the explicit $H^{(1)}$ and noting that integrals of mixed (xy etc.) terms will vanish, we get

$$E^{(2)}_{1s1s} \approx -\frac{1}{e^2/a_0} \frac{e^4}{R^6} \langle \psi^{(0)}_{1s1s} | x^2_{a1} x^2_{b2} + y^2_{a1} y^2_{b2} + 4z^2_{a1} z^2_{b2} | \psi^{(0)}_{1s1s} \rangle.$$

These integrals can be calculated, giving

$$E^{(2)}_{1s1s} \approx -\frac{6e^2 a^5_0}{R^6}.$$

The exact expression may be obtained by summing over states, giving to three decimals

$$E^{(2)}_{1s1s} = -\frac{6.499 e^2 a^5_0}{R^6}.$$

A "dynamic" explanation: the dipole moment of an atom vanishes on average, but may exist momentarily. If we ignore the correlation between the moments of the two atoms we get zero interaction between the average moments, which is reflected by the vanishing of the first-order correction. However, one dipole moment affects the orientation of the other, which gives a second-order effect.